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Asymmetric Synthesis of Vicinal Thioether Alcohols by Diastereoselective 1,2-Addition of Carbon Nucleophiles to Enantiomerically Enriched α-Sulfenylated Aldehydes

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Abstract: Optically active α-sulfenylated aldehydes (*S*)-**1**, readily available by asymmetric alkylation of α-sulfenylated acetaldehyde-SAMP-hydrazones followed by chemoselective oxidative removal of the chiral auxiliary, can be transformed into vicinal thioether alcohols **2**, **5** and **6** by diastereoselective 1,2-addition using various carbon nucleophiles. The final compounds are obtained with high enantiomeric- (*ee* = 80 - 97%) and diastereomeric excesses (*de* = 88 - > 95%) in good chemical yields (51 - 88%).

Due to the importance of vicinal thioether alcohols as synthetic intermediates, several groups have been engaged with their diastereo- and enantioselective synthesis during the last two decades[1].

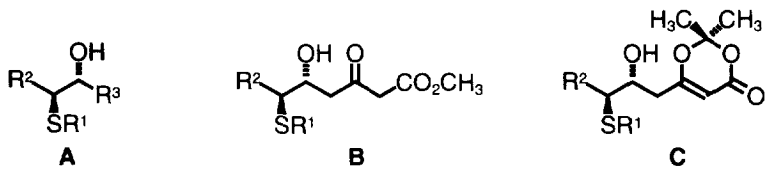
Starting with racemic α-sulfenylated aldehydes or ketones, these efforts have included the nucleophilic addition of organometallic reagents[2], hydride reductions[2b] and Lewis acid promoted addition of allylmetal reagents[3] and enol ethers[4] to furnish racemic vicinal thioether alcohols with high levels of diastereoselectivity. The stereochemical outcome of the reactions were found to be dependent upon both the groups on sulfur and the Lewis acid.

By employing enantiopure ferrocenylaminoalcohols as chiral catalyst, Butsugan *et al.*[2c] were able to achieve high levels of asymmetric induction in the diastereo- and enantioselective addition of dialkylzinc reagents to racemic α-thioaldehydes. Furthermore, Warren *et al.*[4f] reported the kinetic resolution in *anti* aldol reactions with racemic α-phenylthioaldehydes and chiral boron enolates. The use of optically pure sulfoxides in diastereoselective alkylations and reductions made it possible for Fujisawa *et al.*[5a] and Solladié *et al.*[5b] to furnish vicinal thioalcohols with high enantiomeric excesses which were converted to biologically active epoxides. Alternatively, Craig *et al.*[5c] explored the synthetic utility of racemic vinylic sulfoxides in Pummerer-rearrangements to afford after reduction α-phenylthio alcohols with good chemical yields.

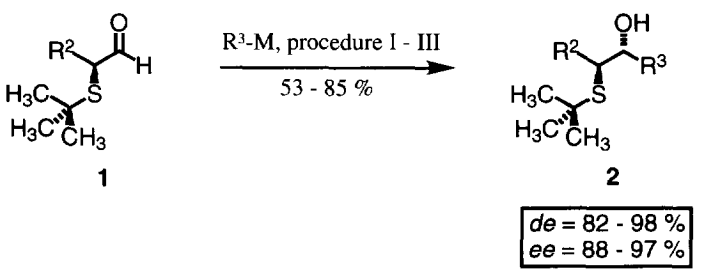
An asymmetric approach to α-thioether alcohols *via* diastereoselective Michael addition of mercaptans to chiral 5-alkoxy-2(5H)-furanones followed by $LiAlH_4$ reduction was published by Feringa *et al.*[6a]. Later, Sato *et al.*[6b] successively applied a similar strategy *via* cuprate addition to chiral 5-alkoxy-3-phenylthio-2(5H)-furanones.

By diastereoselective addition of various methylmetal reagents to chiral thiomethylketones, Fujisawa *et al.*[6c] furnished both diastereomers of vicinal thioether alcohols, which were converted to epoxides and vicinal diols respectively. Finally, Schneider and Goergens[7] described the lipase catalysed resolution of 1-*t*-butylthio-2-alcohols *via* the corresponding chloroacetates. The enantiomeric excesses were reported to be > 96%. However, all mentioned asymmetric methodologies lack a general applicability, being restricted to certain substitution patterns.

As we have previously described, optically active α-sulfenylated aldehydes can be efficiently prepared by asymmetric α-alkylation of α-sulfenylated acetaldehyde-SAMP-hydrazones or by direct α-sulfenylation of aldehyde-SAMP-hydrazones followed by chemoselective oxidative cleavage of the chiral auxiliary[8]. This methodology has now been extended to the diastereo- and enantioselective synthesis of various vicinal thioether alcohols *via* diastereoselective 1,2-addition of different nucleophiles to enantiomerically enriched α-sulfenylated aldehydes. We wish to report in detail the results of these investigations for the synthesis of β-sulfenylated alcohols of type **A**, **B** and **C**.



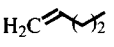
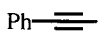
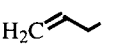
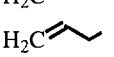
Starting with commercially available α-bromoacetaldehyde diethylacetal the chiral aldehydes **1a** - **f** were prepared in 5 steps with good overall yields (30 - 73%) and high enantioselectivities (*ee* = 80 - 94%). The application of three different procedures (I-III, see experimental) rendered it possible to carry out additions of alkyl-, aryl- and allyl-moieties in a highly diastereoselective manner (Scheme 1). Table 1 summarises the examples of this protocol.



Scheme 1. Asymmetric synthesis of vicinal thioether alcohols by 1,2-addition of organometallic reagents to α-sulfenylated aldehydes

Several points are noteworthy. In general, the observed diastereoselectivities are high (*de* > 94%) the only exceptions being additions with methyl- and allyl-Grignard reagents (82% and 46% *de*). The last problem could be solved by applying the boron trifluoride mediated addition of allyl-tri-(*n*-butyl)stannane[12]. Thus we achieved a considerable enhancement of diastereoselectivity (*de* = 92%). In all cases the enantiomeric excess decreased only slightly (max. 5%) due to the basic reaction conditions. The determination of the *ee*-values could be carried out by converting the chiral alcohols to the corresponding diastereomeric carbamates using (*S*)-methylbenzylisocyanates[10] or (*S*)-MTPA-chloride[11] followed by ^{1}H and ^{13}C NMR spectra analyses.

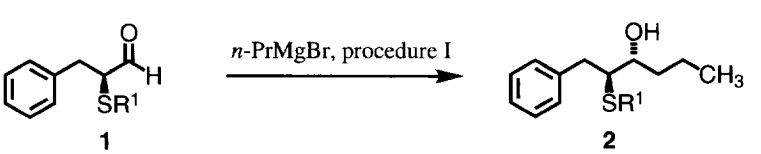
Table 1. Enantiomerically enriched vicinal thioether alcohols **2**

Starting material	*ee* [%][a]	R^2	R^3	M	Product[b]	Yield [%][c]	$[\alpha]_D^{22}$ (*c*, $CHCl_3$)	*de* [%][d]	*ee* [%][e]
1a	97	*n*-Pr	Bn	MgBr	**2a**	54	+ 6.7 (1.0)	98	97
1b	95	*i*-Pr	Bn	MgBr	**2b**	68	+ 6.2 (1.6)	97	95
1c	92	$C_6H_{11}CH_2$	Bn	MgBr	**2c**	53	− 1.2 (0.6)	98	92
1c	92	$C_6H_{11}CH_2$	*n*-Pr	MgBr	**2d**	57	+ 16.1 (1.3)	95	89
1c	92	$C_6H_{11}CH_2$		MgBr	**2e**	57	+ 12.0 (0.9)	95	90
1d	92	Bn	Me	MgBr	**2f**	84	+ 28.3 (1.0)	82	92
1d	92	Bn	*n*-Pr	MgBr	**2g**	55	+ 34.6 (1.0)	96	90
1d	92	Bn	$C_6H_{11}CH_2$	MgBr	**2h**	77	+ 34.9 (0.8)	97	92
1d	92	Bn	*i*-Pr	MgBr	**2i**	53	+ 8.7 (0.9)	94	88
1d	92	Bn	Ph	MgBr	**2j**	62	+ 69.8 (1.0)	95	92
1d	92	Bn		Li	**2k**[f]	62	+ 153.8 (0.9)	95	90[g]
1d	92	Bn		MgBr	**2l**	51	+ 52.2 (1.9)	46	87
1d	92	Bn		$Sn(n\text{-}Bu)_3$	**2l**[h]	67	+ 72.5 (1.2)	92	91

a) Determined after converting to the corresponding SASP-hydrazone by HPLC according to ref.[9]; b) following procedure I; c) after flash chromatography; d) determined by gas chromatography of the crude product; e) determined by ^1H and ^{13}C NMR spectroscopy on the corresponding carbamates after reaction with (S)-methylbenzylamine[10]; f) following procedure II; g) determined by ^1H and ^{13}C NMR spectroscopy on the corresponding Mosher ester[11]; h) following procedure III.

Conjecturing that the diastereoselectivity should be dependent on the group R^1 attached to sulfur, we examined the addition of *n*-propyl magnesium bromide to α-sulfenylated (*S*)-3-phenylpropanal (Table 2), bearing different thioether groups.

Table 2. Effect of the thio substituent R^1 on the diastereoselectivity

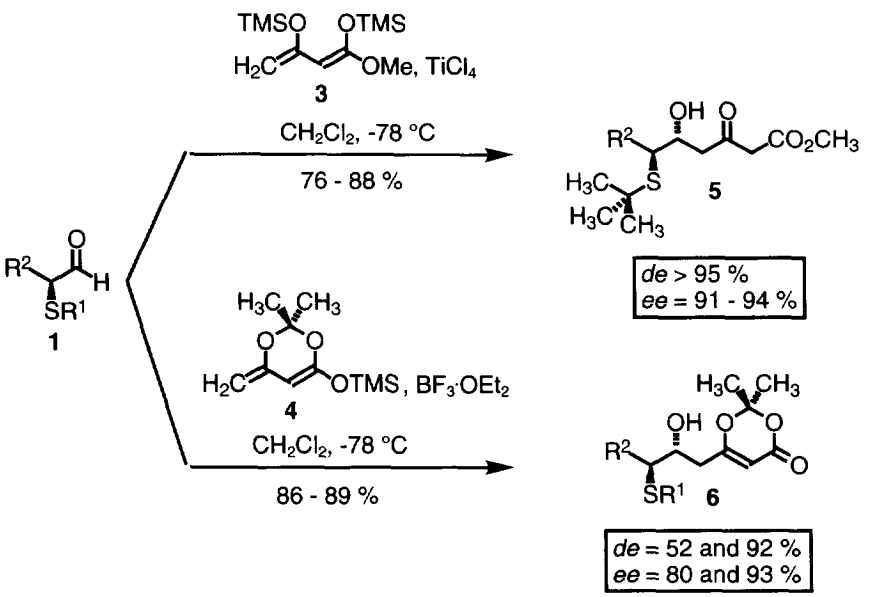


1 **2**

R^1	Yield [%]	*anti* : *syn*
t-Bu	55	98 : 2
i-Pr	63	87 : 13
Ph	54	95 : 5
Bn	58	91 : 9

As a result, one can conclude that the *t*-butyl- and phenyl thio moiety exhibits the highest levels of diastereoselectivity. With other groups on sulfur such as Bn or *i*-Pr the addition becomes considerably less selective.

The assignment of the relative stereochemistry was based on the conversion of the thioalcohols **2** to the corresponding epoxides[13]. Judging from the value of the vicinal epoxide coupling constants (J = 2 - 2.5 Hz) characteristic for *trans*-epoxides[14], we concluded that the nucleophilic addition proceeds in a *trans*-selective manner. This result is in complete accordance with those reported in the literature[2a - c]. To further demonstrate the synthetic utility of α-thioaldehydes **1** we investigated the Lewis acid mediated addtion of acetoacetate-d^4-reagents **3**[15] and **4**[16] (Scheme 2).



Scheme 2. Asymmetric synthesis of vicinal thioether alcohols **5** and **6** *via* 1,2-addition of acetoacetate-d^4-reagents **3** and **4** to α-sulfenylated aldehydes **1**.

The simultaneous addition of the α-*t*-butylthioaldehydes **1** and titanium tetrachloride to 1-methoxy-1,3-bis-(trimethylsilyloxy)butadiene (**3**) in dichloromethane at −78 °C (see experimental) afforded after flash column chromatography pure 5-hydroxy-6-*t*-butylthio-3-oxoesters **5** with high diastereoselectivities and good chemical yields. Furthermore 6-substituted dioxins **6** could be obtained by boron trifluoride mediated addition of 2,2-dimethyl-4-methylene-6-trimethylsilyloxy-dioxin (**4**) to α-thioaldehydes **1d** and **1f** (Table 3).

These results deserve some comment. The addition of **3** or **4** to *t*-butylthioaldehydes generally occurred with high stereoselectivity (*de* > 92%) and good chemical yields (76 - 88%). On the other hand, addition of **4** to α-phenylthioaldehyde **1f** proceeded with a significantly lower stereoselectivity (*de* = 52%). The enantiomeric excesses and relative stereochemistry of compounds **5** could be scrutinized after *syn*-reduction of the 3-keto-moiety and subsequent acetalisation by ^{1}H NMR shift experiments using (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoro-ethanol[17] as chiral cosolvent (6eq.) and N.O.E. experiments, respectively.

Table 3. Optically active 3-oxo-esters **5** and 6-substituted dioxin-4-ones **6**.

Starting material	*ee* [%][a]	R^1	R^2	Product	Yield [%][b]	$[\alpha]_D^{22}$ (*c*, $CHCl_3$)	*de* [%][c]	*ee* [%]
1a	91	*t*-Bu	*n*-Pr	**5a**	88	+ 31.3 (1.0)	> 95	91[d]
1b	91	*t*-Bu	*i*-Pr	**5b**	76	+ 25.6 (1.0)	> 95	91[d]
1d	93	*t*-Bu	Bn	**5c**	87	+ 52.0 (1.2)	> 95	93[d]
1e	94	*t*-Bu	DCBn[e]	**5d**	81	+ 45.1 (1.3)	> 95	94[d]
1d	93	*t*-Bu	Bn	**6a**	86	+ 52.8 (0.8)	92	93[f]
1f	80	Ph	*i*-Pr	**6b**	89	− 22.5 (1.2)	52	80[f]

a) Determined by ^1H and ^{13}C NMR spectroscopy on the Mosher esters[11] derived from the corresponding alcohols after $LiAlH_4$-reduction; b) after flash column chromatography; c) determined by ^{13}C NMR spectroscopy; d) determined after *syn*-reduction and acetalisation with 2,2-dimethoxypropane by ^1H NMR spectroscopy with (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol[17] as chiral cosolvent (6eq.); e) DCBn: 2,4-dichlorobenzyl; f) determined after lactonisation and *O*-alkylation with dimethyl sulfate by ^1H NMR spectroscopy with (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.).

For the corresponding determination of the relative and absolute configurations of compounds **6**, these were lactonized (K_2CO_3/MeOH)[18] and regioselectively *O*-alkylated with dimethyl sulfate in acetone. The subsequent ^1H NMR shift and N.O.E. experiments, as described above, resulted in an exact determination of *ee*-values and relative stereochemistry. In conclusion, no racemisation was observed during the reaction sequence.

As can be seen from the reported results, the sense of diastereoselectivity remains the same no matter of the nature of the Lewis acid. Using the *bis*-silyl enol ether **3**, titanium tetrachloride and the sterically hindered *t*-butylthio moiety, not prone to chelation, the only product to be isolated were the non-chelation-controlled *anti*-isomers of **5**. These observations are in agreement with the general trends reported by Cinquini, Cozzi *et al.*[4a] who investigated several different thio-groups (Me, *i*-Pr, Ph) in Lewis acid mediated additions of silyl enol ethers to racemic α-thioaldehydes. Using titanium tetrachloride, they observed an increase of the non-chelation products in the order MeS < *i*-PrS < PhS, confirming that the sterically less demanding methyl group gives rise to higher yields of chelation products than *i*-Pr- or Ph-groups. On the other hand, using the silyl enol ether **4** together with the non-chelating boron trifluoride etherate the degree of *anti*-stereoselectivity was high for α-*t*-butylthio-aldehyde **1d** (92%), whereas in the case of α-phenylthio aldehyde **1f** only 52% *de* in favour of the *anti*-isomer could be achieved. This result is in marked contrast to those of the Italian group[4a], who using boron trifluoride etherate observed generally high levels of *anti*-diastereoselectivity independent of the silyl enol ether and the nature of the thio group. Thus, as a consequence the nucleophilic and Lewis acid mediated additions to α-*t*-butylthioaldehydes generally give rise to a high degree of *anti* diastereoselection. These results can be rationalised by application of the Felkin-Anh model[19], with the thio group playing the role as the large electronegative substituent.

In summary, starting from readily available α-*t*-butylthio aldehydes, the diastereoselective 1,2-addition of various carbon nucleophiles allows a practical and flexible entry into vicinal thioether alcohols of high enantiomeric (*ee* > 88%) and diastereomeric purity (de > 88%). Further applications of this methodology are under current investigation within our laboratories.

EXPERIMENTAL

General. All reactions were carried out using standard Schlenk techniques unless otherwise stated. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran and diethyl ether were freshly distilled from potassium, dichloromethane from CaH_2 under argon. Light petroleum refers to the fraction with b.p. 40 - 80 °C. Reagents of commercial quality were used from freshly opened containers unless otherwise stated. Allyltri(*n*-butyl)stannane was purchased from Acros Chimica, Belgium; *n*-butyllithium (1.6 M in *n*-hexane), titanium tetrachloride and magnesium-turnings were purchased from Merck, Darmstadt. Allyl bromide was freshly distilled and handled under argon.

Apparatus. Analytical TLC: Merck glass-backed silica gel 60 F_{254} plates. - Preparative column chromatography: Merck silica gel 60, particle size 0.040 - 0.063 mm (230 - 400 mesh) (flash). - Analytical GC: Siemens Sichromat 2 or 3 equipped with a SE-54-CB-column (25 m x 0.25 mm), carrier gas nitrogen, FID. - Optical rotations: Perkin-Elmer P 241 polarimeter; solvents of Merck UVASOL quality unless otherwise stated. - IR spectra: Perkin-Elmer 1420 and Perkin-Elmer FT/IR 1750. - ^1H NMR spectra (300 MHz), ^{13}C NMR spectra (75 MHz): Varian VXR 300 and Gemini 300 (solvent: $CDCl_3$, TMS as internal standard). - Mass spectra: Varian MAT 212 (EI 70 eV) (relative intensities in parentheses). - Microanalyses: Heraeus CHN-O-Rapid.

General procedure for the addition of organometallic compounds to (S)-2-sulfenylated aldehydes **1** *(Procedure I):*

A flame dried Schlenk flask was charged with magnesium turnings (0.18 g; 7.5 mmol), suspended in diethyl ether (20 ml) under argon and cooled to 0 °C. After addition of the corresponding alkyl halide (7.5 mmol) the mixture was stirred until a clear solution was obtained. A solution of the chiral (*S*)-2-sulfenylated aldehyde **1**[8a] in diethyl ether (1 ml) was then added *via* syringe and stirring was continued overnight at room temperature. After hydrolysis with saturated ammonium chloride solution (10 ml) the mixture was transferred to a separating funnel together with diethyl ether (30 ml) and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether (20 ml) and the combined organic phase was washed with brine, dried over $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* and purification by column chromatography afforded pure thioether alcohols **2** as colourless liquids or solids, respectively.

*Procedure for the addition of phenylalkynyllithium to (S)-2-t-butylthio-3-phenylpropanal (***1d***) (Procedure II):*

A flame dried Schlenk flask was charged with *n*-butyl lithium (1.7 ml; 2.7 mmol) in THF (5 ml) at 0 °C. A solution of TMEDA (0.41 ml; 2.7 mmol) in THF (10 ml) was then added dropwise and stirred for 10 minutes. After addition of phenylacetylene (0.30 ml; 2.7 mmol) the mixture was allowed to stir for a further 10 minutes. The resulting dark solution was cooled to –30 °C and a solution of aldehyde (*S*)-**1d**[8a] (0.50 g; 2.3 mmol) in THF (1 ml) was added. After warming overnight the reaction mixture was hydrolysed with brine (15 ml), charged to a separating funnel together with diethyl ether (30 ml) and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether (20 ml) and the combined organic phase are washed with brine, dried over $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* and purification by column chromatography afforded pure thioether alcohol (*S,R*)-**2k** as a colourless liquid.

*Procedure for the addition of allyl-tri-(n-butyl)stannane to (S)-2-t-butylthio-3-phenylpropanal (**1d**) (Procedure III):*

A flame dried Schlenk flask was charged with a solution of α-thioaldehyde (*S*)-**1d**[8a] (0.30 g; 1.35 mmol) in dichloromethane (5 ml) and $BF_3{\cdot}OEt_2$ (0.20 ml; 1.35 mmol) was added at 0 °C. After cooling to −78 °C, allyl-tri-(*n*-butyl)stannane (0.66 g; 2 mmol) was added dropwise and the reaction mixture was stirred for 2 h at the same temperature. After hydrolysis with saturated sodium hydrogencarbonate solution (10 ml), the mixture was transferred to a separating funnel together with diethyl ether (30 ml) and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether (20 ml) and the combined organic phase was washed with potassium fluoride solution and brine, dried over $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* and purification by column chromatography afforded pure thioether alcohol (*S,R*)-**2l** as a colourless liquid.

*General procedure for the titanium tetrachloride mediated addition of 1-methoxy-1,3-bis-(trimethylsilyloxy)butadiene (**3**) to (S)-2-thioaldehydes (Procedure IV):*

A flame dried Schlenk flask was charged with a solution of 1-methoxy-1,3-*bis*-(trimethylsilyloxy)butadiene (**3**)[15] (2.34 g; 9.0 mmol) in dichloromethane (30 ml) and cooled to −78 °C. After simultaneous dropwise addition of the corresponding α-thioaldehyde **1**[8a,e] (3.0 mmol in 12.4 ml dichloromethane) and titanium tetrachloride solution (12.4 ml in dichloromethane; 6.2 mmol; c = 0.5 M) *via* motorized syringe pumps, the dark reaction mixture was stirred for a further 30 minutes and methanol (3 ml) was added. The orange mixture was transfered to a separating funnel together with diethyl ether (300 ml) and pH-7 buffer and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether (50 ml) and the combined organic phase was washed with brine, dried over $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* and purification by column chromatography afforded pure thioether alcohol (*R,S*)-**5** as colourless oils.

*General procedure for the boron trifluoride etherate mediated addition of 2,2-dimethyl-4-methylene-6-trimethylsilyloxydioxin (**4**) to α-thioaldehydes (S)-**1d** and (S)-**1f** (Procedure V):*

A flame dried Schlenk flask was charged with a solution of the (*S*)-**1d**[8a] or (*S*)-**1f**[8e] (2 mmol) in dichloromethane (10 ml) and cooled to −78 °C. After dropwise addition of boron trifluoride etherate (0.62 ml; 4.2 mmol) and further stirring for 10 minutes, a solution of 2,2-dimethyl-4-methylene-6-trimethylsilyloxydioxin (**4**)[16] (1.07 g; 5 mmol in 5 ml of dichloromethane) was added dropwise. After stirring for a further 1 h, the orange solution was transfered to a separating funnel together with diethyl ether (50 ml) and pH-7 buffer and the organic layer was separated. The aquous layer was extracted twice with diethyl ether (50 ml) and the combined organic phase was washed with brine, dried over $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* and purification by column chromatography afforded pure thioether alcohol (*R,S*)-**6** as colourless oils.

(2R,3S)-3-t-Butylthio-1-phenylhexan-2-ol [(*R,S*)-**2a**]: 54% Yield from aldehyde **1a**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.52 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +6.7 (*c* = 1.0, $CHCl_3$). - *de* = 98%, determined by GC-analysis of the crude product. - *ee* = 97%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 − 3200 (m, br., OH), 3020 (m, $CH_{arom.}$), 2980 - 2820 (s), 1595 (m), 1480 (m), 1370 (m), 1190 (s), 1080 - 1020 (s) cm^{-1}. - ^1H NMR: δ = 0.94 (t, *J* = 7.1 Hz, 3H, CH_3), 1.29 (s, 9H, $SC(CH_3)_3$), 1.25 - 1.80 (m, 4H,

CH_2CH_2), 2.39 (d, J = 6.3 Hz, 1H, CHO*H*), 2.68 - 2.78 (m, 2H, CHOHCH_2), 2.81 (td, J = 12.7 Hz/ 4.9 Hz, 1H, CHS), 4.01 (m, 1H, C*H*OH), 7.17 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 14.16 (CH_3), 20.67 (5-CH_2), 31.75 (SC(CH_3)$_3$), 33.91 (4-CH_2), 39.76 (1-CH_2), 43.41 (S*C*(CH_3)$_3$), 49.29 (3-CH), 75.07 (2-CH), 126.33 (CH_{meta}), 128.47 (CH_{ortho}), 129.29 (CH_{para}), 139.06 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 266 (2) [M^+], 248 (17) [M^+–H_2O], 159 (62) [248–$C_7H_7^+$], 145 (24) [$C_4H_8SC(CH_3)_3^+$], 119 (13), 91 (29) [$C_7H_7^+$], 89 (81) [$C_4H_8SH^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_{16}H_{26}OS$ (266.44): calcd. C 72.14, H 9.84; found C 72.25, H 9.83.

(2R,3S)-3-t-Butylthio-4-methyl-1-phenylpentan-2-ol [(*R,S*)-**2b**]: 68% Yield from aldehyde **1b**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.59 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +6.2 (c = 1.6, $CHCl_3$). - *de* = 97%, determined by GC-analysis of the crude product. - *ee* = 95%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3060, 3020 (m, $CH_{arom.}$), 2960, 2870 (s), 1610 (m), 1495 (m), 1450 (s), 1380 (m), 1365 (m), 1160 (s), 1070 (s), 1030 (s), 910 (m) cm^{-1}. - ^{1}H NMR: δ = 1.03 (t, J = 6.7 Hz, 3H, CH_3), 1.04 (t, J = 6.7 Hz, 3H, CH_3), 1.31 (s, 9H, SC(CH_3)$_3$), 2.18 (septd, J = 6.7 Hz/ 5.4 Hz, 1H, CH), 2.40 (d, J = 5.7 Hz, 1H, CHO*H*), 2.60 (dd, J = 5.4 Hz/ 4.7 Hz, 1H, CHS), 2.70 (dd, J = 13.7 Hz/ 9.4 Hz, 1H, C*H*H'), 3.00 (dd, J = 13.7 Hz/ 4.0 Hz, 1H, CH*H'*), 4.01 (dddd, J = 9.4 Hz/ 5.7 Hz/ 4.7 Hz/ 4.0 Hz, 1H, C*H*OH), 7.20 - 7.34 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 20.03 (CH_3), 21.78 (CH_3), 29.03 (4-CH), 32.05 (SC(CH_3)$_3$), 40.22 (1-CH_2), 43.12 (S*C*(CH_3)$_3$), 55.69 (3-CH), 74.99 (2-CH), 126.26 (CH_{meta}), 128.43 (CH_{ortho}), 129.19 (CH_{para}), 139.31 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 266 (1) [M^+], 248 (23) [M^+–H_2O], 205 (35) [248–$C_3H_7^+$], 159 (55) [248–$C_7H_7^+$], 145 (10), 91 (35) [$C_7H_7^+$], 89 (85) [$C_4H_8SH^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_{16}H_{26}OS$ (266.44): calcd. C 72.14, H 9.84; found C 72.09, H 9.83.

(2R,3S)-3-t-Butylthio-4-cyclohexyl-1-phenylbutan-2-ol [(*R,S*)-**2c**]: 53% Yield from aldehyde **1c**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.51 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = –1.2 (c = 0.6, $CHCl_3$). - *de* = 98%, determined by GC-analysis of the crude product. - *ee* = 92%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3300 (m, br., OH), 3050, 3020 (m, $CH_{arom.}$), 2940 - 2820 (s), 1595 (m), 1490 (m), 1460 - 1440 (m), 1360 (s), 1360, 1160 (s), 1080 (s), 1030 (s) cm^{-1}. - ^{1}H NMR: δ = 0.80 - 1.06 (m, 2H, (8-CH_2), 1.10 - 1.35 (m, 3H, C*H*CH_2), 1.29 (s, 9H, SC(CH_3)$_3$), 1.40 - 1.78 (m, 8H, 6-CH_2, 7-CH_2), 2.44 (d, J = 6.4 Hz, 1H, CHO*H*), 2.73 - 2.75 (m, 2H, CHOHCH_2), 2.89 (dt, J = 5.7 Hz/ 3.0 Hz, 1H, CHS), 4.04 (ddt, J = 6.4 Hz/ 3.0 Hz/ 1.0 Hz, 1H, C*H*OH), 7.18 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 26.21 (8-CH_2), 26.32, 26.62 (7-CH_2), 31.74 (SC(*C*H_3)$_3$), 33.32, 33.78 (6-CH_2), 34.66 (5-CH), 39.20 (4-CH_2), 39.51 (1-CH_2), 43.48 (S*C*(CH_3)$_3$), 46.75 (3-CH), 74.82 (2-CH), 126.28 (CH_{meta}), 128.39 (CH_{ortho}), 129.26 (CH_{para}), 138.90 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 320 (2) [M^+], 302 (15) [M^+–H_2O], 214 (11), 213 (62) [302–SC(CH_3)$_3^+$], 199 (19), 173 (11), 143 (100) [$C_6H_{11}CH_2CHSH^+$], 121 (15) [$C_6H_5CH_2CHOH^+$], 117 (16), 109 (59), 91 (35) [$C_7H_7^+$], 83 (16), 67 (17), 57 (82) [$C(CH_3)_3^+$]. - $C_{20}H_{32}OS$ (320.53): calcd. C 74.94, H 10.06; found C 74.90, H 10.17.

(2S,3R)-2-t-Butylthio-1-cyclohexylhexan-3-ol [(*S,R*)-**2d**]: 57% Yield from aldehyde **1c**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.58 (light petroleum / diethyl ether,

4:1). - $[\alpha]_D^{20}$ = +16.1 (*c*= 1.3, $CHCl_3$). - *de* = 95%, determined by GC-analysis of the crude product. - *ee* = 89%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3500 – 3200 (m, br., OH), 2980 - 2820 (s), 1600 (m), 1455 (m), 1120 (s), 1060 (s), 1010 (s) cm^{-1}. - ^1H NMR: δ = 0.83 - 0.98 (m, 5H, CH_3, 10-CH_2), 1.10 - 1.58 (m, 10H, CH_3CH_2, 8-CH_2, 9-CH_2), 1.33 (s, 9H, $SC(CH_3)_3$), 1.68 - 1.81 (m, 5H, $CHCH_2$, $CHOHCH_2$), 2.20 - 2.45 (m, 1H, CHO*H*), 2.92 (dt, *J* = 6.4 Hz/ 3.3 Hz, 1H, CHS), 3.75 (ddt, *J* = 6.7 Hz/ 3.3 Hz/ 2.0 Hz, 1H, C*H*OH) ppm. - ^{13}C NMR: δ = 14.12 (CH_3), 19.38 (5-CH_2), 26.19 (10-CH_2), 26.27, 26.62 (9-CH_2), 31.80 ($SC(CH_3)_3$), 33.47, 33.53 (8-CH_2), 34.63 (7-CH), 39.97 (4-CH_2), 43.26 ($SC(CH_3)_3$), 47.68 (2-CH), 72.49 (3-CH) ppm. - MS (70 eV), *m/z* (%): 272 (7) [M^+], 200 (12), 199 (31) [$C_6H_{11}CH_2CHSC(CH_3)_3^+$], 144 (15), 143 (100) [$199^+-C_4H_8$], 142 (12) [$C_6H_{11}CH_2CHS^+$], 110 (17), 83 (16), 81 (9), 67 (13), 57 (85) [$C(CH_3)_3^+$]. - $C_{16}H_{32}OS$ (272.49): calcd. C 70.52, H 11.83; found C 70.81, H 11.90.

(2S,3R)-2-t-Butylthio-1-cyclohexylhept-6-en-3-ol [(*S,R*)-**2e**]: 57% Yield from aldehyde **1c**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.60 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +12.0(*c*= 0.9, $CHCl_3$). - *de* = 95%, determined by GC-analysis of the crude product. - *ee* = 90%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 2920 - 2840 (s), 1640 (m), 1450 (m), 1390 (s), 1360 (m), 1160, (s), 1060 (s), 1000 (s) cm^{-1}. - ^1H NMR: δ = 0.78 - 1.02 (m, 2H, 13-CH_2), 1.10 - 1.35 (m, 4H, 12-CH_2), 1.33 (s, 9H, $SC(CH_3)_3$), 1.38 - 1.56 (m, 4H,11-CH_2), 1.60 - 1.81 (m, 5H, $CHCH_2$, H_2C=$CHCH_2$), 2.13 (ddt, *J* = 14.8 Hz/ 6.7 Hz/ 6.4 Hz, 1H, CHOHC*H*H'), 2.28 (ddt, *J* = 14.8 Hz/ 6.7 Hz/ 6.4 Hz, 1H, CHOHCH*H*'), 2.38 (d, *J* = 7.7 Hz, 1H, CHO*H*), 2.93 (dt, *J* = 6.4 Hz/ 3.3 Hz, 1H, CHS), 3.74 (m, 1H, C*H*OH), 4.97 (ddt, *J* = 10.2 Hz/ 2.0 Hz/ 1.0 Hz, 1H, $H_{cis}H_{trans}C$=C*H*), 5.05 (ddt, *J* = 17.1 Hz/ 2.0 Hz/ 1.6 Hz, 1H, $H_{cis}H_{trans}C$=CH), 5.83 (dddd, *J* = 17.1 Hz/ 10.2 Hz/ 6.9 Hz/ 6.7 Hz, 1H, $H_{cis}H_{trans}C$=CH) ppm. - ^{13}C NMR: δ = 26.18 (13-CH_2), 26.26, 26.61 (12-CH_2), 30.33 (5-CH_2), 31.80 ($SC(CH_3)_3$), 31.89 (1-CH_2), 33.49 (11-CH_2), 34.62 (10-CH), 40.11 (4-CH_2), 43.34 ($SC(CH_3)_3$), 47.62 (2-CH), 71.96 (3-CH), 114.85 (7-CH_2), 138.45 (6-CH) ppm. - MS (70 eV), *m/z* (%): 284 (1) [M^+], 199 (30) [$C_6H_{11}CH_2CHSC_4H_9^+$], 177 (15), 143 (100) [$199^+-C_4H_8$], 142 (11) [$C_6H_{11}CH_2CHS^+$], 110 (17) [$C_6H_{11}CH{=}CH_2$], 109 (49), 83 (17), 81 (16), 67 (20), 57 (72) [$C(CH_3)_3^+$]. - $C_{17}H_{32}OS$ (284.50): calcd. C 71.77, H 11.35; found C 71.64, H 11.23.

(2S,3R)-2-t-Butylthio-1-phenylbutan-2-ol [(*S,R*)-**2f**]: 84% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.55 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +28.3 (*c* = 1.0, $CHCl_3$). - *de* = 82%, determined by GC-analysis of the crude product. - *ee* = 92%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3500 – 3200 (m, br., OH), 3060, 3020 (m, $CH_{arom.}$), 2960 - 2820 (s), 1600 (m), 1490 (m), 1450 (s), 1375 (m), 1160 (m), 1120 (s),1070 (s), 960 (m) cm^{-1}. - ^1H NMR: δ = 1.18 (d, *J* = 6.4 Hz, 3H, CH_3), 1.21 (s, 9H, $SC(CH_3)_3$), 2.10 - 2.25 (m, 1H, CHO*H*), 2.84 (dd, *J* = 14.0 Hz/ 8.5 Hz, 1H, C*H*H'), 2.90 (dd, *J* = 14.0 Hz/ 7.0 Hz, 1H, CH*H*'), 3.03 (ddd, *J* = 8.5 Hz/ 7.0 Hz/ 3.6 Hz, 1H, CHS), 3.83 (qd, *J* = 6.4 Hz/ 3.6 Hz, 1H, C*H*OH), 7.17 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 18.76 (CH_3), 31.49 ($SC(CH_3)_3$), 40.64 (1-CH_2), 43.28 ($SC(CH_3)_3$), 53.14 (2-CH), 67.73 (3-CH), 126.41 (CH_{meta}), 128.34 (CH_{ortho}), 129.29 (CH_{para}), 139.39 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 238 (20) [M^+], 147 (14) [$M^+-C_7H_7^+$], 138 (20), 137 (63), 104 (9), 91 (52) [$C_7H_7^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_{14}H_{22}OS$ (238.39): calcd. C 70.53, H 9.30; found C 70.55, H 9.54.

(2S,3R)-2-t-Butylthio-1-phenylhexan-3-ol [(*S,R*)-**2g**]: 55% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.59 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +34.6 (*c* = 1.0, $CHCl_3$). - *de* = 96%, determined by GC-analysis of the crude product. - *ee* = 90%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3060 (m, $CH_{arom.}$), 2980 - 2860 (s), 1600 (m), 1490 (m), 1455 (m), 1375 (m), 1160 (s), 1120 (m), 1040 (s) cm^{-1}. - ^1H NMR: δ = 1.16 (s, 9H, $SC(CH_3)_3$), 1.18 (t, *J* = 7.0 Hz, 3H, CH_3), 1.28 - 1.66 (m, 4H, CH_2CH_2), 2.26 (d, *J* = 8.5 Hz, 1H, CHO*H*), 2.78 - 3.05 (m, 3H, $C_6H_5CHH'CHS$),3.55 (m, 1H, C*H*OH), 7.16 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 14.06 (CH_3), 19.28 (5-CH_2), 31.43 ($SC(CH_3)_3$), 34.83 (4-CH_2), 39.51 (1-CH_2), 43.37 ($SC(CH_3)_3$), 52.66 (2-CH), 72.18 (3-CH), 126.33 (CH_{meta}), 128.26 (CH_{ortho}), 129.40 (CH_{para}), 139.62 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 266 (12) [M^+], 194 (19) [$C_6H_5CH_2$-$CH_2SC_4H_9^+$], 138 (42) [$194^+-C_4H_8$], 137 (83) [$194^+-C_4H_9$], 119 (54), 104 (16), 91 (26) [$C_7H_7^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_{16}H_{26}OS$ (266.44): calcd. C 72.14, H 9.84; found C 72.44, H 9.78.

(2S,3R)-2-t-Butylthio-4-cyclohexyl-1-phenyl-butan-3-ol [(*S,R*)-**2h**]: 77% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.62 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +34.9 (*c* = 0.8, $CHCl_3$). - *de* = 97%, determined by GC-analysis of the crude product. - *ee* = 92%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3060 (m, $CH_{arom.}$), 2980 - 2840 (s), 1600 (m), 1490 (m), 1450 (m), 1360 (m), 1160 (s), 1120 (m), 1040 (s) cm^{-1}. - ^1H NMR: δ = 0.70 - 1.77 (m, 13H, $C_6H_{11}CHH'$), 1.20 (s, 9H, $SC(CH_3)_3$), 2.23 (d, *J* = 9.1 Hz, 1H, CHO*H*), 2.85 - 2.88 (m, 2H, C_6H_5CHH'), 3.01 (ddd, *J* = 8.4 Hz/ 7.1 Hz/ 3.4 Hz, 1H, CHS), 3.75 (m, 1H, C*H*OH), 7.16 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 26.18 (8-CH_2), 26.46, 26.66 (7-CH_2), 31.46 ($SC(CH_3)_3$), 32.52 (7-CH_2), 34.00 (5-CH), 34.66 (7-CH_2), 39.93 (4-CH_2), 40.34 (1-CH_2), 43.35 ($SC(CH_3)_3$), 53.04 (2-CH), 69.49 (3-CH), 126.36 (CH_{meta}), 128.26 (CH_{ortho}), 129.36 (CH_{para}), 139.54 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 320 (21) [M^+], 229 (42) [$M^+-C_7H_7$], 194 (59) [$C_6H_5CH_2$-$CH_2SC_4H_9^+$], 173 (56), 147 (35), 139 (15), 138 (98) [$194^+-C_4H_8$], 137 (89) [$194^+-C_4H_9$], 136 (21), 104 (15), 91 (41) [$C_7H_7^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_{20}H_{32}OS$ (320.53): calcd. C 74.94, H 10.06; found C 74.85, H 9.87.

(2S,3R)-2-t-Butylthio-4-methyl-1-phenylpentan-3-ol [(*S,R*)-**2i**]: 53% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.55 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +8.7 (*c* = 0.9, $CHCl_3$). - *de* = 94%, determined by GC-analysis of the crude product. - *ee* = 88%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3060, 3020 (m, $CH_{arom.}$), 2980 - 2840 (s), 1600 (m), 1490 (s), 1450 (s), 1360 (m), 1160 (s), 1120 (m), 1040 (s) cm^{-1}. - ^1H NMR: δ =1.02 (d, *J* = 6.7 Hz, 3H, CH_3), 1.05 (s, 9H, $SC(CH_3)_3$), 1.08 (d, *J* = 6.4 Hz, 3H, CH_3), 1.92 (m, 1H, C*H*$(CH_3)_2$), 2.20 - 2.45 (m, br, 1H, CHO*H*), 2.54 (dd, *J* = 14.4 Hz/ 11.4 Hz, 1H, C_6H_5CHH'), 2.97 - 3.07 (m, 2H, C_6H_5CHH', CHS), 3.43 (dd, *J* = 8.7 Hz/ 2.7 Hz, 1H, C*H*OH), 7.16 - 7.31 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 19.14, 20.12 (5-CH_3), 31.23 ($SC(CH_3)_3$), 35.06 (4-CH), 43.49 ($SC(CH_3)_3$), 50.28 (2-CH), 80.95 (3-CH), 126.05 (CH_{meta}), 127.93 (CH_{ortho}), 129.84 (CH_{para}), 140.20 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 266 (10) [M^+], 194 (16) [$C_6H_5CH_2CH_2SC_4H_9^+$], 157

(11), 138 (32) [194$^+$–C_4H_8], 137 (61) [194$^+$–C_4H_9], 119 (28), 104 (12), 101 (9), 91 (26) [$C_7H_7^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_{16}H_{26}OS$ (266.44): calcd. C 72.12, H 9.83; found C 72.20, H 10.15.

(1R,2S)-2-t-Butylthio-1,3-diphenylpropan-1-ol [(*R,S*)-**2j**]: 62% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.54 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +69.8 (*c* = 1.0, $CHCl_3$). - *de* = 95%, determined by GC-analysis of the crude product. - *ee* = 92%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3300 (m, br., OH), 3080, 3030 (m, $CH_{arom.}$), 2980, 2920, 2860 (s), 1605 (m), 1495 (m), 1455 (m), 1370 (m), 1220 (m), 1175 (s), 1155 (m), 1055 (s) cm^{-1}. - ^{1}H NMR: δ =1.14 (s, 9H, $SC(CH_3)_3$), 2.50 (dd, *J* = 14.4 Hz/ 10.0 Hz, 1H, C_6H_5CH*H*'), 2.76 (dd, *J* = 14.4 Hz/ 4.4 Hz, 1H, C_6H_5CH*H*'), 3.01 (d, *J* = 4.4 Hz, 1H, CHO*H*), 3.17 (ddd, *J* = 10.0 Hz/ 4.4 Hz/ 4.0 Hz, 1H, CHS), 4.99 (dd, *J* = 4.4 Hz/ 4.0 Hz, 1H, C*H*OH), 7.03 - 7.46 (m, 10H, C_6H_5) ppm. - ^{13}C NMR: δ = 31.30 ($SC(CH_3)_3$), 36.42 (3-CH_2), 43.69 ($SC(CH_3)_3$), 53.58 (2-CH), 75.96 (1-CH), 126.05, 126.29 (CH_{meta}), 127.45, 127.93 (CH_{ortho}), 128.22, 129.59 (CH_{para}), 139.80, 141.22 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 300 (0.2) [M$^+$], 194 (25) [$C_6H_5CH_2CH_2SC_4H_9^+$], 138 (20) [194$^+$–C_4H_8], 137 (100) [194$^+$–C_4H_9], 107 (17), 104 (16), 91 (30) [$C_7H_7^+$], 79 (16), 77 (16) [$C_6H_5^+$], 57 (94) [$C(CH_3)_3^+$]. - $C_{19}H_{24}OS$ (300.46): calcd. C 75.95, H 8.05; found C 76.05, H 8.00.

(3R,4S)-4-t-Butylthio-1,5-diphenylpent-1-yn-3-ol [(*R,S*)-**2k**]: 62% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.58 (light petroleum / diethyl ether, 4:1). - mp.: 89 - 90 °C. - $[\alpha]_D^{20}$ = +153.8 (*c* = 0.9, $CHCl_3$). - *de* = 95%, determined by GC-analysis of the crude product. - *ee* = 90%, determined after derivatisation with (*S*)-MTPA-Cl. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3060, 3030 (m, $CH_{arom.}$), 2970, 2900 (s), 2220 (m), 1595 (m), 1545 (m), 1490 (m), 1455 (m), 1440 (m), 1370 (m), 1320 (m), 1190 (s), 1160 (m), 1055 (s), 940 (m), 910 (m) cm^{-1}. - ^{1}H NMR: δ = 1.31 (s, 9H, $SC(CH_3)_3$), 1.40 - 1.70 (m, br., 1H, CHO*H*), 3.09 (dd, *J* = 14.1 Hz/ 5.4 Hz, 1H, C_6H_5CH*H*'), 3.12 (m, 1H, CHS), 3.21 (dd, *J* = 14.1 Hz/ 10.7 Hz, 1H, C_6H_5CH*H*'),4.55 (d, *J* = 3.0 Hz, 1H, C*H*OH), 7.22 - 7.55 (m, 10H, C_6H_5) ppm. - ^{13}C NMR: δ = 31.51 ($SC(CH_3)_3$), 41.76 (5-CH_2), 43.65 ($SC(CH_3)_3$), 52.54 (4-CH), 63.57 (3-CH), 86.20 (2-C), 87.52 (1-C), 126.68, 126.72 (CH_{meta}), 128.26, 128.51 (CH_{ortho}), 129.26, 131.88 (CH_{para}), 138.77, 138.95 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 324 (3) [M$^+$], 285 (13), 268 (13) [M$^+$–C_4H_8], 193 (26), 138 (11), 137 (100) [193$^+$–C_4H_8], 103 (8), 91 (18) [$C_7H_7^+$], 77 (16) [$C_6H_5^+$], 57 (60) [$C(CH_3)_3^+$]. - $C_{21}H_{24}OS$ (324.48): calcd. C 77.73, H 7.45; found C 77.88, H 7.37.

(2S,3R)-2-t-Butylthio-1-phenylhex-5-en-3-ol [(*R,S*)-**2l**]: 67% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.57 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +72.5, *c* = 1.2, $CHCl_3$). - *de* = 92%, determined by GC-analysis of the crude product. - *ee* = 91%, determined after derivatisation with (*S*)-α-methylbenzylisocyanate. - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3060 (m, $CH_{arom.}$), 2940, 2860 (s), 1640 (m), 1600 (m), 1495 (m), 1450 (m), 1375 (m), 1160 (s), 1000 (s), 920 (m) cm^{-1}. - ^{1}H NMR: δ = 1.16 (s, 9H, $SC(CH_3)_3$), 2.18 - 2.32 (m, br., 1H, CHO*H*), 2.36 - 2.48 (m, 2H, C_6H_5CHH'), 2.75 - 2.87 (m, 1H, CHOHC*H*H'), 2.93 - 3.00 (m, 1H, CHOHCH*H*'), 3.01 (dt, *J* = 6.4 Hz/ 3.3 Hz, 1H, CHS), 3.76 (ddt, *J* = 7.7 Hz/ 3.3 Hz/ 1.3 Hz, 1H, C*H*OH), 5.09 - 5.20 (m, 2H, $H_{cis}H_{trans}C$=C*H*), 5.87 (ddt, J = 17.1 Hz/ 10.0 Hz/ 7.0 Hz, 1H, $H_{cis}H_{trans}C$=CH), 7.17 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 31.38 ($SC(CH_3)_3$), 37.72 (4-CH_2), 38.94 (1-CH_2), 43.56 ($SC(CH_3)_3$), 51.76

(2-CH), 72.44 (3-CH), 117.38 (6-CH_2), 126.33 (CH_{meta}), 128.16 (CH_{ortho}), 129.5 (CH_{para}), 135.13 (5-CH), 139.45 (C_{ipso}) ppm. - MS (70 eV), *m/z* (%): 266 (3) [M^++2], 199 (31), 177 (15), 144 (14), 143 (100), 110 (15), 109 (49), 83 (17), 81 (15), 67 (19), 57 (69) [$C(CH_3)_3^+$]. - $C_{16}H_{24}OS$ (264.43): calcd. C 72.67, H 9.15; found C 72.67, H 9.12.

(5R,6S)-6-t-Butylthio-5-hydroxy-3-oxo-nonanoic acid methyl ester [(*R,S*)-**5a**]: 88% Yield from aldehyde **1a**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.10 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +31.3 (*c* = 1.0, CH_2Cl_2). - *de* > 95%, determined by NMR spectroscopy. - *ee* = 91%, determined after *syn*-reduction and acetalisation with 2,2-dimethoxypropane by ^{1}H-NMR spectroscopy with (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.). - IR (film): $\tilde{\nu}$ = 3600 − 3200 (m, br., OH), 2960, 2902, 2872 (s), 1748, 1716 (vs, C=O), 1655, 1631 (m, C=C [enol]), 1460 (s), 1438 (s), 1406 (s), 1366 (s), 1325 (s, br.), 1263 (s, br.), 1241 (s, br.), 1200 (s, br.), 1161 (s, br.), 1098 (s), 1069 (s), 1043 (s, br.), 1016 (s, br.), 860 (m, br.), 805 (m, br.) cm^{-1}. - ^{1}H NMR: δ = 0.93 (t, *J* = 7.1 Hz, 3H, CH_3), 1.34 (s, 9H, $SC(CH_3)_3$), 1.48 - 1.62 (m, 3H, CH_3CHH', $CHH'CHS$), 2.72 - 2.87 (m, 4H, $CHOHCHH'$, $CHH'CHS$), 3.55 (m, 2H, $CHH'CO_2CH_3$), 3.75 (s, 3H, CO_2CH_3), 4.23 (ddd, *J* = 12.6 Hz/ 6.6 Hz/ 4.4 Hz, 1H, *CH*OH) ppm. - ^{13}C NMR: δ = 14.09 (CH_3), 20.29 (8-CH_2), 31.75 ($SC(CH_3)_3$), 34.88 (7-CH_2), 43.64 ($SC(CH_3)_3$), 46.45 (4-CH_2), 48.91 (6-CH), 49.75 (2-CH_2), 52.38 (OCH_3), 69.48 (5-CH), 167.47 (1-C=O), 202.35 (3-C=O) ppm. - MS (70 eV), *m/z* (%): 290 (17) [M^+], 272 (9) [M^+–H_2O], 216 (6) [272^+–C_4H_8], 203 (5), 198 (11), 169 (7) [M^+–CH_3OH–$SC(CH_3)_3$], 145 (91) [$C_6H_9O_4^+$ and $C_8H_{17}S^+$], 113 (20) [$C_5H_5O_3^+$], 101 (16), 89 (100) [145^+–C_4H_8], 71 (6), 57 (98) [$C(CH_3)_3^+$], 55 (23). - $C_{14}H_{26}O_4S$ (290.42): calcd. C 57.90, H 9.02; found C 57.60, H 9.08.

(5R,6S)-6-t-Butylthio-5-hydroxy-7-methyl-3-oxo-octaoic acid methyl ester [(*R,S*)-**5b**]: 76% Yield from aldehyde **1b**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.19 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +25.6 (*c* = 1.0, CH_2Cl_2). - *de* > 95%, determined by NMR spectroscopy. - *ee* = 91%, determined after *syn*-reduction and acetalisation with 2,2-dimethoxypropane by ^{1}H-NMR spectroscopy with (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.). - IR (film): $\tilde{\nu}$ = 3700 − 3200 (m, br., OH), 2960 (vs), 2871 (s), 1747, 1717 (vs, C=O), 1654, 1630 (m, C=C [enol]), 1461 (s), 1438 (s), 1405 (s), 1384 (s), 1365 (s), 1325 (s, br.), 1266 (s, br.), 1240 (s, br.), 1202 (s, br.), 1161 (s, br., sh), 1095 (m, br.), 1066 (m, sh.), 1039 (m, br.), 1014 (m, br.), 922 (w, sh), 863 (m, br.), 812 (m, br.), 740 (m, br.) cm^{-1}. - ^{1}H NMR: δ = 1.00 (t, *J* = 6.6 Hz, 3H, CH_3), 1.03 (t, *J* = 6.9 Hz, 3H, CH_3), 1.34 (s, 9H, $SC(CH_3)_3$), 2.02 (qqd, *J* = 6.9 Hz/ 6.6 Hz/ 5.2 Hz, 1H, $(CH_3)_2CH$), 2.61 (dd, *J* = 5.8 Hz/ 5.2 Hz, 1H, CHS), 2.77 (dd, J = 16.5 Hz/ 9.3 Hz, 1H, $CHOHCHH'$), 2.96 (dd, J = 16.5 Hz/ 3.3 Hz, 1H, $CHOHCHH'$), 2.98 (d, br., *J* = 5.8 Hz, 1H, CHO*H*), 3.54 (s, 2H, $CHH'CO_2CH_3$), 3.75 (s, 3H, CO_2CH_3), 4.21 (dddd, *J* = 9.8 Hz/ 5.8 Hz/ 5.2 Hz/ 3.3 Hz, 1H, *CH*OH) ppm. - ^{13}C NMR: δ = 19.55 (CH_3), 21.35 (CH_3), 29.45 (7-CH), 32.07 ($SC(CH_3)_3$), 43.33 ($SC(CH_3)_3$), 47.23 (4-CH_2), 49.75 (2-CH_2), 52.38 (OCH_3), 54.94 (6-CH), 69.33 (5-CH), 167.47 (1-C=O), 202.35 (3-C=O) ppm. - MS (70 eV), *m/z* (%): 290 (3) [M^+], 272 (1) [M^+–H_2O], 203 (1), 200 (1) [M^+–$(CH_3)_3CSH$], 198 (2) [216^+–H_2O], 169 (3) [M^+–CH_3OH–$SC(CH_3)_3$], 145 (55) [$C_6H_9O_4^+$ and $C_8H_{17}S^+$], 113 (10) [$C_5H_5O_3^+$], 101 (13), 89 (100) [145^+–C_4H_8], 71 (6), 57 (95) [$C(CH_3)_3^+$], 55 (15), 43 (30), 41 (16). - $C_{14}H_{26}O_4S$ (290.42): calcd. C 57.90, H 9.02; found C 57.59, H 8.87.

(5R,6S)-6-t-Butylthio-5-hydroxy-3-oxo-7-phenylheptanoic acid methyl ester [(*R,S*)-**5c**]: 87% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.44 (light petroleum / diethyl ether, 1:2). - $[\alpha]_D^{20}$ = +52.0 (*c* = 1.2, CH_2Cl_2). - *de* > 95%, determined by NMR spectroscopy. - *ee* = 93%, determined after *syn*-reduction and acetalisation with 2,2-dimethoxypropane by ^{1}H-NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.). - IR (film): $\tilde{\nu}$ = 3700 – 3200 (m, br., OH), 3085, 3061, 3028 (m, $CH_{arom.}$), 2958, 2927, 2899, 2863 (s), 1950, 1870 (w, $C{=}C_{arom.}$), 1747, 1718 (vs, C=O), 1654, 1631 (m, C=C [enol]), 1495 (m), 1455 (s), 1439 (s), 1406 (s, sh), 1366 (s), 1325 (s, br.), 1262 (s, br.), 1205 (s, br.), 1162 (vs, br.), 1115 (m, br.), 1077 (m, br.), 1031 (s, br., sh.), 933 (w, br., sh), 860 (w, br., sh), 810 (w, br.), 753 (m), 702 (s) cm^{-1}. - ^{1}H NMR: δ = 1.18 (s, 9H, $SC(CH_3)_3$), 2.76 (dd, J = 16.5 Hz/ 9.1 Hz, 1H, CHOHC*H*H'), 2.79 - 3.01 (m, 3H, CHOHCH*H'*, C_6H_5CHH'), 3.02 (ddd, *J* = 8.2 Hz/ 6.3 Hz/ 4.4 Hz, 1H, CHS), 3.48 (s, 2H, $CHH'CO_2CH_3$), 3.73 (s, 3H, CO_2CH_3), 4.17 (m, 1H, C*H*OH), 7.20 - 7.32 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 31.37 ($SC(CH_3)_3$), 39.42 (7-CH_2), 43.86 ($SC(CH_3)_3$), 46.45 (4-CH_2), 49.55 (2-CH_2), 50.81 (6-CH), 52.39 (OCH_3), 69.23 (5-CH), 126.52 (CH_{meta}), 128.31 (CH_{ortho}), 129.56 (CH_{para}), 138.91 (C_{ipso}), 167.43 (1-C=O), 202.22 (3-C=O) ppm. - MS (70 eV), *m/z* (%): 338 (10) [M$^+$], 320 (7) [M$^+$–H_2O], 264 (2) [320$^+$–C_4H_8], 247 (10) [M$^+$–C_7H_7], 230 (7) [M$^+$–H_2O–$HSC(CH_3)_3$], 193 (17) [M$^+$–$C_6H_9O_4$], 173 (58) [247$^+$–H_2O– C_4H_8], 159 (8), 145 (19) [$C_6H_9O_4^+$], 137 (77), 117 (6), 113 (12) [M$^+$–CH_3OH–$C_{12}H_{17}S$], 104 (10), 101 (12), 91 (35) [$C_7H_7^+$], 57 (100) [$C(CH_3)_3^+$], 43 (21), 41 (22). - $C_{18}H_{26}O_4S$ (338.46): calcd. C 63.88, H 7.74; found C 64.20, H 8.01.

(5R,6S)-6-t-Butylthio-5-hydroxy-3-oxo-7-(2,4-dichlorophenyl)-heptanoic acid methyl ester [(*R,S*)-**5d**]: 81% Yield from aldehyde **1e**[8e] after column chromatography (silica gel, light petroleum / diethyl ether, 4:1). - R_f = 0.13 (light petroleum / diethyl ether, 4:1). - $[\alpha]_D^{20}$ = +45.1 (*c* = 1.3, CH_2Cl_2). - *de* > 95%, determined by NMR spectroscopy. - *ee* = 94%, determined after *syn*-reduction and acetalisation with 2,2-dimethoxypropane by ^{1}H-NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.). - IR (film): $\tilde{\nu}$ = 3700 – 3200 (m, br., OH), 3090, 3063, 3027 (w, $CH_{arom.}$), 2957, 2899, 2862, 2719 (s), 1747, 1716 (vs, C=O), 1654, 1632 (m, C=C [enol]), 1588 (s), 1561 (m), 1495 (vs), 1474 (s), 1460 (s), 1439 (s), (s), 1405 (s), 1390 (s), 1366 (s), 1325 (s, br.), 1256 (s, br.), 1203 (s, br.), 1161 (s, br.), 1102 (s), 1078 (s, br.), 1050 (s, sh.), 1011 (m, br.), 951 (w, br.), 929 (w), 865 (m, sh), 822 (m, br.), 764 (w, br.), 701 (w, br.) cm^{-1}. - ^{1}H NMR: δ = 1.06 (s, 9H, $SC(CH_3)_3$), 2.60 (dd, *J* = 13.5 Hz/ 10.2 Hz, 1H, $C_6H_3Cl_2CHH'$), CHOHC*H*H'), 2.84 - 2.96 (m, 2H, CHOHC*HH'*), 3.05 (ddd, *J* = 10.2 Hz/ 4.4 Hz/ 3.8 Hz, 1H, CHS), 3.15 (dd, *J* = 13.5 Hz/ 4.4 Hz, 1H, $C_6H_3Cl_2CHH'$), 3.55 (s, br., 2H, $CHH'CO_2CH_3$), 3.75 (s, 3H, CO_2CH_3), 4.29 (m, 1H, C*H*OH), 7.18 (dd, *J* = 8.2 Hz/ 1.9 Hz, 1H, ClC=C*H*-CH), 7.24 (d, br., *J* = 8.2 Hz, 1H, ClC=CH-C*H*), 7.35 (d, *J* = 1.9 Hz, 1H, ClC=C*H*-CCl) ppm. - ^{13}C NMR: δ = 31.18 ($SC(CH_3)_3$), 35.30 (7-CH_2), 43.79 ($SC(CH_3)_3$), 46.53 (4-CH_2), 48.11 (6-CH), 49.66 (2-CH_2), 52.44 (OCH_3), 70.72 (5-CH), 126.62 (CH-CH_{meta}), 128.98 (CH_{ortho}), 133.02 (CCl_{para}), 134.04 (CCl-CH_{meta}), 134.75 (CCl_{ortho}), 135.30 (C_{ipso}), 167.41 (1-C=O), 201.95 (3-C=O) ppm. - MS (70 eV), *m/z* (%): 407 (0.1) [M$^+$], 371 (18) [M$^+$–Cl], 315 (4) [371$^+$–C_4H_8], 297 (13) [315$^+$–H_2O], 261 (5) [$C_{12}H_{15}Cl_2S^+$], 205 (18) [261$^+$–C_4H_8], 173 (37) [M$^+$–H_2O–$C_7H_5Cl_2$], 159 (15) [$C_7H_5SCl_2^+$], 145 (22) [$C_6H_9O_4^+$], 113 (12) [M$^+$–

CH_3OH–$C_{12}H_{15}SCl_2$], 101 (14), 57 (100) [$C(CH_3)_3$)$^+$], 43 (23), 41 (20). - $C_{18}H_{24}O_4SCl_2$ (407.35): calcd. C 53.10, H 5.94; found C 53.08, H 6.17.

(2'R,3'S)- 2,2-Dimethyl-6-[3'-t-butylthio-2'-hydroxy-4'-phenylbut-1'-yl]-1,3-dioxin-4-one [(*R,S*)-**6a**]: 86% Yield from aldehyde **1d**[8a] after column chromatography (silica gel, light petroleum / diethyl ether, 2:1). - R_f = 0.27 (light petroleum / diethyl ether, 2:1). - $[\alpha]_D^{20}$ = +52.8 (*c* = 0.8, CH_2Cl_2). - *de* = 92%, determined by NMR spectroscopy. - *ee* = 93%, determined after lactonisation and *O*-alkylation with dimethyl sulfate by ^{1}H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.). - IR (film): $\tilde{\nu}$ = 3500 – 3200 (m, br., OH), 3082, 3062, 3026, 3002 (s, $CH_{arom.}$), 2974, 2963, 2939, 2899, 2858 (s), 1947, 1865 (m, C-$C_{arom.}$), 1707 (vs, br., sh, C=O), 1636 (vs, sh, C=C), 1494 (s), 1470 (s), 1455 (s), 1438 (s), 1421 (s), 1392 (vs, br.), 1375 (vs, sh), 1341 (s), 1326 (s), 1308 (m), 1283 (s), 1256 (s), 1206 (vs), 1182 (s), 1152 (s), 1084 (s), 1072 (s), 1057 (m), 1027 (s), 1018 (s), 1006 (s), 967 (m), 935 (m), 908 (s), 879 (m), 862 (m), 840 (m), 810 (vs), 708 (s, sh), 701 (s) cm^{-1}. - ^{1}H NMR: δ = 1.21 (s, 9H, $SC(CH_3)_3$), 1.67 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.27 (dd, *J* = 14.6 Hz/ 10.2 Hz, 1H, CHOHC*H*H'), 2.53 (dd, *J* = 14.6 Hz/ 3.0 Hz, 1H, CHOHCH*H*'), 2.58 (m, 1H, CHO*H*), 2.86 (dd, *J* = 14.0 Hz/ 8.0 Hz, 1H, C_6H_5C*H*H'), 2.92 (dd, *J* = 14.0 Hz/ 7.6 Hz, 1H, C_6H_5CH*H*'), 3.06 (ddd, *J* = 8.0 Hz/ 7.6 Hz/ 3.8 Hz, 1H, CHS), 3.95 (m, 1H, C*H*OH), 5.32 (s, 1H, C=CH), 7.19 - 7.36 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 24.21 (CH_3), 25.73 (CH_3), 31.34 ($SC(CH_3)_3$), 37.46 (4'-CH_2), 40.31 (1'-CH_2), 43.95 ($SC(CH_3)_3$), 51.84 (3'-CH), 69.20 (2'-CH), 95.35 (5-CH), 106.63 (2-C), 126.71 (CH_{meta}), 128.42 (CH_{ortho}), 129.32 (CH_{para}), 138.54 (C_{ipso}), 161.04 (4-C=O), 169.18 (6-C=O) ppm. - MS (70 eV), *m/z* (%): 364 (8) [M$^+$], 306 (9) [M$^+$–CH_3COCH_3], 288 (24) [M$^+$–H_2O–CH_3COCH_3], 250 (10) [306$^+$–C_4H_8], 232 (30) [288$^+$–C_4H_8], 199 (6), 193 (8) [$C_{12}H_{17}S^+$], 188 (7), 159 (34), 137 (63) [193$^+$–C_4H_8], 113 (24) [306$^+$–$C_{12}H_{17}S$], 104 (12) 91 (44) [$C_7H_7^+$], 84 (10), 69 (22), 59 (47), 57 (100) [$C(CH_3)_3$)$^+$], 43 (23), 41 (29). - $C_{20}H_{28}O_4S$ (364.50): calcd. C 65.90, H 7.74; found C 66.10, H 7.85.

(2'R,3'S)- 2,2-Dimethyl 6-[3'-phenylthio-2'-hydroxy-4'-methylpent-1'-yl]-1,3-dioxin-4-one [(*R,S*)-**6b**]: 89% Yield from aldehyde **1f**[8e] after column chromatography (silica gel, light petroleum / diethyl ether, 2:1). - R_f = 0.21 (light petroleum / diethyl ether, 2:1). - $[\alpha]_D^{20}$ = –22.5 (*c* = 1.2, CH_2Cl_2). - *de* = 52%, determined by NMR spectroscopy. - *ee* = 80%, determined after lactonisation and *O*-alkylation with dimethyl sulfate by ^{1}H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent (6eq.). - IR (film): $\tilde{\nu}$ = 3600 – 3200 (m, br., OH), 3078, 3060, 3015 (m, $CH_{arom.}$), 2963, 2872 (m), 1950, 1875 (w, br., C-$C_{arom.}$), 1718 (vs, C=O), 1634 (s, C=C), 1584 (m), 1480 (m), 1462 (m), 1439 (s), 1392 (s), 1378 (s), 1277 (s, br.), 1258 (s), 1216 (s, sh), 1128 (m), 1088 (m), 1062 (m, br.), 1018 (s), 965 (m), 906 (m), 875 (m), 808 (m) cm^{-1}. - ^{1}H NMR: δ = 1.06 (d, *J* = 6.6 Hz, 3H, C*H*$_3$CH), 1.30 (d, *J* = 6.6 Hz, 3H, C*H*$_3$CH), 1.66 (s, br., 6H, CH_3), 2.21 (m, 1H, CH_3C*H*), 2.29 (dd, *J* = 14.5 Hz/ 9,9 Hz, 1H, CHOHC*H*H'), 2.70 (dd, br., *J* = 14.5 Hz/ 3.0 Hz, 1H, CHOHCH*H*'), 2.87 (s, br., 1H, CHO*H*), 3.02 (dd, *J* = 6.3 Hz/ 5.5 Hz, 1H, CHS), 4.68 (m, 1H, C*H*OH), 5.13 (s, br., 1H, C=CH), 7.18 - 7.48 (m, 5H, C_6H_5) ppm. - ^{13}C NMR: δ = 19.11, 21.50 (5'-CH_3), 24.46, 25.47 (CH_3), 29.34 (4'-CH), 38.56 (1'-CH_2), 64.42 (3'-CH), 69.75 (2'-CH), 95.20 (5-CH), 106.68 (2-C), 126.88 (CH_{meta}), 129.15 (CH_{ortho}), 131.08 (CH_{para}), 136.38 (C_{ipso}), 161.27 (4-C=O), 169.57 (6-C=O) ppm. - MS (70 eV), *m/z* (%): 336 (18) [M$^+$], 278 (39) [M$^+$–CH_3COCH_3], 260 (32) [M$^+$–H_2O–CH_3COCH_3], 194 (12), 191 (15), 169 (6) [278$^+$–C_6H_5S], 167 (12), 166 (74), 165 (100)

$[C_{10}H_{13}S^+]$, 151 (95) $[260^+-C_6H_5S]$, 123 (50) $[151^+-CO]$, 113 (60) $[C_5H_5O_3^+]$, 110 (26), 109 (19) $[C_6H_5S^+]$, 87 (14), 85 (11), 69 (43), 65 (10), 57 (14), 55 (48), 45 (14), 43 (33), 41 (20). - $C_{18}H_{24}O_4S$ (336.45): calcd. C 64.26, H 7.19; found C 64.15, H 7.34.

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